Letters to the Editor

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Crystal and molecular structure of piperidine hydrochloride

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The structure of piperidine in the form of its different hydrohalides has been undertaken by us as a part of our major program on the structure and functions of biomolecules. The present communication deals with the structure determination of piperidine hydrochloride by heavy atom technique

Single crystals were grown by slow evaporation of an aqueous solution of this compound at room temperature. The crystals thus grown are needle shaped, the needle axis being parallel to *b*-axis. The unit cell dimensions as revealed by Weissenberg, oscillation and rotation photographs taken about *b*- and *a*-axes, using CuKα radiation are :

$$a = 9.68\text{Å}$$
$$b = 7.40\text{Å}$$
$$c = 9.67\text{Å}$$
$$\alpha = \beta = \gamma = 90^\circ$$

Systematic absences of reflections in Weissenberg photographs indicate that the space group may be either *Pbcm* or $Pbc2_1$. Three dimensional analysis at a later stage confirmed that the space group is *Pbcm*. Density data ($\rho_m = 1.14$ gm/cc, $\rho_{cal} = 1.16$ gm/cc) indicate that there are four formula units ($C_5H_{11}N.HCl$) per unit cell. Multiple-film equi-inclination Weissenberg technique was used to record intensities on layers *h*0*l* to *h*6*l* and 0*kl*. The position of the heavy atom (chlorine) in the unit cell was located from three dimensional Patterson synthesis. Three dimensional Fourier synthesis was computed with the phase of the heavy atom on CDC 3600 at T.I.F.R., Bombay, using the program written by Blount. A spoke and bead model was constructed which satisfied the stereochemistry.

Refinement was carried out by the method of full matrix least squares using the modified (Srikanta) program of Busing, Martin & Levy (1962) with isotropic temperature factors. The discrepancy factor $R = \dfrac{\Sigma \, | \, |F_0| - |F_c| \, |}{\Sigma |F_0|}$ at this stage was 0.14.

The structure was further refined using individual anisotropic temperature factors for the non-hydrogen atoms, R-value at this stage being 0.11. A three-dimensional difference Fourier synthesis using all the reflections revealed the hydrogen atom positions. Structure factor calculations including the hydrogen atoms were carried out and the final value is 0.094. The atomic parameters and anisotropic temperature factors for the atoms are given in table 1 and intramolecular bond lengths and bond angles are given in table 2. The

TABLE 1

a) Atomic parameters

Atom	x/a	y/b	z/c
Cl	0.17334	0.03633	0.25
N	0.14296	0.45723	0.25
C(1)	0 34090	0.49669	0.11550
C(2)	0.19292	0.54043	0.12009
C(3)	0.40814	0.58508	0.25
C(1′)	0.34690	0.49669	0.38450
C(2′)	0.19292	0.54043	0.37991

*b) Anisotropic temperature coefficients**

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.00546	0.00980	0.00923	−0.00015	0.0000	0.0000
N	0.00418	0.02505	0.00327	−0.00078	0 0000	0 0000
C(1)	0 01202	0.03416	0 01866	0 00378	0 00188	0.00137
C(2)	0.01064	0.03139	0.00765	0.00592	−0.00049	0.00123
C(3)	0.00684	0 01344	0.03608	0.00312	0.0000	0.0000

* In the expression $T = \exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl]$

TABLE 2. Intramolecular bond lengths and bond angles

Bond length (Å)		Bond angle (degree)	
Cl—N	3.088	Cl—N—C(2)	112
N—C(2)	1.478	N—C(2)—C(1)	105
C(1)—C(2)	1.525	C(2)—C(1)—C(3)	105
C(1)—C(3)	1.569	C(1)—C(3)—C(1′)	112

piperidine ring has been found to assume a chair configuration. A mirror parallel to *xy* plane at $z = 1/4$ passes through the molecule. Atoms Cl, N, C(3) lie on the mirror and C(1′), C(2′) (figures 1 and 2) are mirror images of C(1) and C(2). The

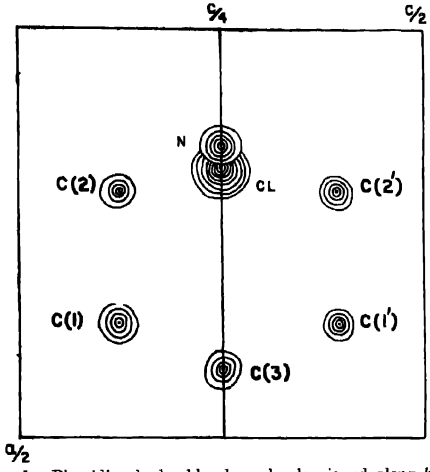

Figure 1. Piperidine hydrochloride molecule viewed along *b*-axis

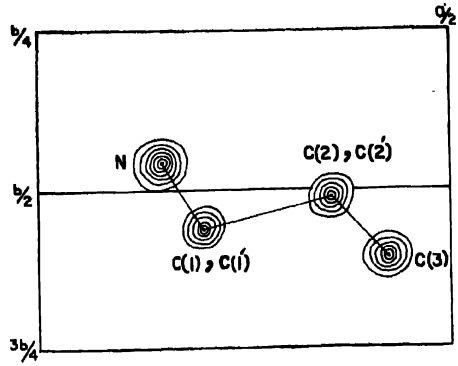

Figure 2. Piperidine hydrochloride molecule viewed along *c*-axis

molecules as viewed down b and c-axes are shown in figure 1 and figure 2, respectively. The molecules are held together by a three-dimensional net work of hydrogen bonds of the type N-H ... Cl, as can be seen from figure 3, a projection down c-axis.

At the final stage of the structural solution of this compound, our attention was drawn to a paper on this compound published by Rerat (1960) with R value of 0.26. In his refinement of the structure, anisotropic temperature factors were not used. The hydrogen atom positions also were not located. His findings, *e.g.* bond lengths and bond angles, differ considerably from ours. The detailed paper will be published elsewhere.

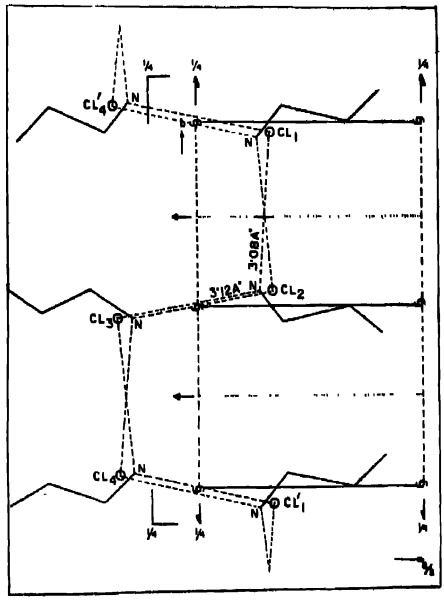

Figure 3. Intermolecular packing projected down c-axis.

References

Busing W. R., Martin, K. O. & Levy H. A. 1962 *Least Squares Refinement (XFLS) Programme*

Rerat Par C. 1960 *Acta Cryst.* **13**, 72,